Chemical Analyses of Sarmatian Glass Beads from Pokrovka, Russia

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The chemical composition of 18 glass beads from Early Sarmatian period burials were determined using electron probe microbeam analysis and energy dispersive X-ray fluorescence. The beads were made from high-magnesia-soda-lime-silica glass, leaded-soda-lime-silica glass, low-magnesia-soda-lime-silica glass and low-magnesia-high-potash glass. Multivariate analysis of the major oxides suggests that there are five distinct glass recipes used to manufacture these beads. These various glass recipes indicate the involvement of the Sarmatians in exchange/trade networks linking the Eastern Mediterranean, the Indian subcontinent, and China.   © 1998 Academic Press

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Introduction

The Sarmatians were a confederation of Indo-Iranian speaking nomads who resided on the Eurasian steppes during the second half of the first millennium BC and into the early centuries AD (Barbarunova, 1995; Lubo-Lesnichenko, 1989:41–43; Melyukova, 1990; Sulimerski, 1970). In the 6th to 4th centuries BC, they were settled on the broad plains around the Volga and in the southern Urals. The began expanding westwards in the 4th century BC, and by the 1st century AD, controlled the steppes between the Dnieper and the Ural mountains. Their confederation was assimilated by the Huns after the 4th century AD.

Previous work by the authors (Hall & Yablonsky, 1997) has demonstrated that the Sarmatians obtained some of their glass from the Black Sea or Eastern Mediterranean regions. The purpose of this paper is to provide further chemical analyses of glass beads found in Sarmatian burials. Additional chemical analyses can provide further information on the exchange and trade networks of the Sarmatians.

Archaeological Materials

All the beads examined in this study came from burials in the Sarmatian cemetery of Pokrovka. Located in

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the Orenburg oblast, Pokrovka is along the Ilek river, south of Sol Iletsk and on the Russian-Kazakhstan border. Joint American-Russian excavations have been conducted here since 1991 (Davis-Kimball & Yablonsky, 1995; Yablonsky, 1993, 1994, 1995).

The beads examined in this study all came from burials dating to the Early Sarmatian period (*c.* 4th century BC to 2nd century BC). Burial 1 from kurgan 8 at Pokrovka cemetery 1 yielded the remains of a female, approximately 27 years old, some round, blue glass beads, pottery, and some gold foil ornaments. Female burials containing glass beads were also found in Pokrovka cemetery 2, kurgan 7, burial 2, Pokrovka cemetery 2, kurgan 23, burial 9 and Pokrovka cemetery 2, kurgan 25, burial 2. A multiple burial consisting of a man and child were found in burial 12 of kurgan 8 in Pokrovka cemetery 2. A bright blue, fragmentary bead was recovered from the burial of a child in Pokrovka cemetery 2, kurgan 23, burial 10.

Some of the beads have parallels to ones found elsewhere in Eurasia. Blue and white eye-beads are common in the "Scythian" burials near the Greek Black Sea colonies and in Sarmatian burials in southern Russia (Alekseeva, 1975; plate 15; Smirnov, 1975: plate 31). The round, blue and yellow beads have been found in other Sarmatian burials along the Ilek river.

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Table 1. Content of the major oxides in the glass beads

Specimen	Na_2O	MgO	Al_2O_3	SiO_2	K_2O	CaO	Fe_2O_3	Colour/shape
P01:K08:B01:01	18·82	2·55	4·60	60·66	3·53	5·41	0·87	blue-round
P01:K08:B01:02	19·11	2·58	4·55	61·16	3·52	5·47	0·84	blue-round
P01:K08:B01:03	18·95	2·79	4·51	61·07	3·54	5·50	0·87	blue-round
P01:K08:B01:04	19·34	2·59	4·55	61·02	3·45	5·31	0·86	blue-round
P01:K08:B01:05	19·06	2·70	4·63	59·80	3·46	5·53	0·86	blue-round
P01:K08:B01:06	19·33	2·70	4·72	61·10	3·58	5·39	0·84	blue-round
P01:K08:B01:07	19·22	2·51	4·60	61·28	3·51	5·53	0·85	blue-round
P01:K08:B01:08	19·45	2·24	4·65	61·04	3·48	5·24	0·87	blue-round
P02:K07:B02:01	13·01	0·36	2·48	73·02	1·57	6·34	1·36	clear-green tint
P02:K07:B02:02	16·10	0·91	2·08	68·64	0·76	7·07	1·15	blue-irregular
P02:K08:B12:01	16·57	0·83	2·02	68·89	0·75	7·32	1·32	eye bead-blue
P02:K23:B09:02	11·44	0·34	1·56	53·30	0·41	2·83	11·68	black
P02:K23:B10:01	0·25	0·35	1·40	72·34	19·59	2·91	0·87	blue-fragment
P02:K25:B02:01	16·39	3·30	1·50	66·10	3·41	6·71	1·35	yellow
P02:K25:B02:02	15·66	3·20	1·51	66·20	3·41	7·02	1·86	yellow
P02:K25:B02:03	15·44	3·18	1·48	66·68	3·44	6·94	1·12	yellow
P02:K25:B02:04	15·89	3·17	1·48	66·80	3·38	7·26	1·27	yellow
P02:K25:B02:05	16·46	3·06	1·48	65·96	3·44	6·67	1·22	yellow

All values were determined using electron probe microbeam analysis (EPMA). All values are in weight percentage.

Methods

Since some of the beads did show some signs of weathering or devitrification, all were cross-sectioned and the resulting surface polished to a 1 μm finish with diamond pastes. The initial material was removed with 600 grit emery paper. The polished surface was the one all analyses were done on.

Electron probe microbeam analysis (EPMA) and energy dispersive X-ray fluorescence (EDXRF) were used to obtain the chemical compositions presented here. Both methods were used since previous work has demonstrated that EDXRF has better detection limits for the transition elements than EPMA, while EPMA has better detection limits and accuracy for the lighter elements such as aluminum (Al), calcium (Ca), potassium (K) and sodium (Na) (Henderson, 1989: 218–219).

The aluminum, calcium, iron (Fe), magnesium (Mg), potassium, sodium and silicon (Si) contents were obtained using an eight spectrometer ARL SEMQ wavelength dispersive electron beam microprobe. The lead (Pb) content was also determined by EPMA when it exceeded 5000 parts per million (ppm). The electron beam voltage was operated at 15 KeV and 30 nA. It was defocused to a diameter of 40 μm. A count time of 10 s was used and the values presented in Table 1 are an average of at least five analyses of a polished surface. The results were quantified using the PROBE, version 3·5 program. The X-ray counts were corrected for deadtime, off-peak background, beam and standard drift and volatization. Interferences were tested and corrected by using the method developed by Donovan, Snyder & Rivers (1993: 23–28). Finally, the concentration was calculated using the corrected X-ray counts and ZAF corrections. Calibration was based on the analyses of the National Bureau of Standards (NBS) K-411 and K-412, US Geological Survey (USGS) MAD-10, pure lead, and synthetic crystals of albite, alumina (Al_2O_3), magnesia (MgO) and silica (SiO_2) of known concentration. The detection limits for the above listed elements under these conditions are estimated to be at 200 ppm to 500 ppm. The analytical accuracy, as defined by Bishop *et al.* (1990: 539), ranges from a low of 0·7% for silicon to a high of 5% for magnesium and sodium.

The EDXRF analyses were performed using a Spectrace 440 EDXRF machine equipped with a rhodium X-ray tube and a Tracor TX 6100 X-ray analyzer. The X-ray tube was operated at 30 kV, 20 mA in vacuum at 250 s livetime to generate X-ray intensities for the other elements. The K_α X-ray intensities were converted to concentration values using a Compton scatter matrix correction and the linear regression of a set of Japan Geological Survey (JGS), NBS, National Institute of Standards and Testing (NIST) and USGS mineral standards. A Lucas-Tooth & Price (1961) correction is used to account for inter-element effects. The detection limits, as determined on geologic standards (Shackley, 1995: 544, 551), are as follows: Co, 14 ppm; Cu, 10 ppm; Ga, 7·8 ppm; Mn, 40 ppm; Nb, 7 ppm; Ni, 10 ppm; Pb, 8 ppm; Rb, 5 ppm; Sr, 3·5 ppm; Th, 9 ppm; Ti, 23 ppm; Y, 7 ppm; Zn, 4 ppm; Zr, 7 ppm. For the concentration levels in this study, the accuracy is 25% or less. Further details on the EDXRF operating conditions for silicic materials can be found in Hall & Yablonsky (1997) or Shackley (1995). All mathematical and statistical results were obtained using SPSS for Windows 3·1.

Results

Composition

The chemical analyses of the glass beads from Pokrovka are in Tables 1 and 2. The silica content ranges from 53% to 74%, the soda (Na_2O) concentration between 0·25% and 20%, and the lime (CaO) concentration ranges between 2·5% and 7·5%.

Table 2. Trace elements found in the glass beads

Specimen	CuO (wt. %)	MnO (wt.%)	PbO (wt. %)	TiO$_2$ (wt. %)	CoO	NbO$_2$	NiO	Rb$_2$O	SrO	Y$_2$O$_3$	ZnO	ZrO$_2$
P01:K08:B01:01	0·779	0·051	0·022	0·269	n.d.	n.d.	n.d.	40	250	10	140	70
P01:K08:B01:02	0·732	0·052	0·023	0·235	n.d.	n.d.	n.d.	30	250	10	130	90
P01:K08:B01:03	0·789	0·058	0·024	0·214	n.d.	n.d.	10	40	270	10	50	90
P01:K08:B01:04	0·756	0·052	0·014	0·269	n.d.	n.d.	n.d.	40	230	10	70	80
P01:K08:B01:05	0·782	0·053	0·020	0·245	n.d.	n.d.	n.d.	30	260	10	121	70
P01:K08:B01:06	0·769	0·052	0·029	0·268	n.d.	n.d.	n.d.	40	260	10	110	70
P01:K08:B01:07	0·780	0·053	0·023	0·254	n.d.	n.d.	n.d.	30	290	10	80	90
P01:K08:B01:08	0·735	0·054	0·016	0·220	n.d.	n.d.	10	40	280	10	80	80
P02:K07:B02:01	0·196	0·032	0·015	0·273	n.d.	10	n.d.	20	480	10	130	140
P02:K07:B02:02	0·151	0·784	0·014	0·126	90	10	20	20	420	10	70	50
P02:K08:B12:01	0·210	0·354	0·118	0·114	230	10	n.d.	10	410	n.d.	70	50
P02:K23:B09:02	0·261	0·030	17·25	0·542	140	n.d.	50	n.d.	170	n.d.	170	180
P02:K23:B10:01	0·018	0·017	0·011	0·153	40	10	60	100	60	10	70	100
P02:K25:B02:01	0·006	0·168	0·002	0·169	n.d.	n.d.	10	20	290	10	50	30
P02:K25:B02:02	0·005	0·187	0·001	0·196	n.d.	10	30	70	270	n.d.	110	40
P02:K25:B02:03	0·008	0·137	0·001	0·180	n.d.	n.d.	40	20	290	n.d.	100	40
P02:K25:B02:04	0·006	0·137	0·002	0·167	n.d.	20	n.d.	20	300	10	130	30
P02:K25:B02:05	0·006	0·155	0·002	0·130	n.d.	20	50	30	310	10	50	40

Except for the lead content in bead P02:K23:B09:02, all values were determined by energy dispersive X-ray fluorescence (EDXRF). The lead content in P02:K23:B09:02 was determined by EPMA. Barium was also searched for in this bead, but not detected. Unless noted, the values listed above are in ppm.
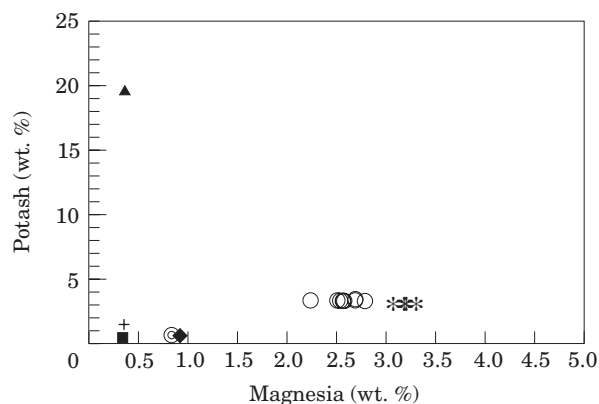

Figure 1. Plot of the magnesia content versus the potash content. Glass with less than 2% K$_2$O and 1% MgO can be classed as low-magnesia (LMG) soda-lime-silica glasses. Glasses with more than 1% MgO are classed as high-magnesia (HMG), soda-lime-silica glasses. Colour: *, yellow; ⊙, eye bead-blue; +, clear-green tint; ◆, blue irregular; ▲, blue-fragment; ○, blue-cylindrical; ■, black.

As implied by the range of the soda content, and evidenced in Figure 1, these six burials yielded four types of glass. Three of the beads have a potash (K$_2$O) content below 2% and a magnesia content below 1%, thus, they can be classed as low-magnesia (LMG) soda-lime silica glasses (Henderson, 1985: 271, 275; Sayre & Smith, 1961, 1967: 281–283). A single fragmentary blue bead (P02:K23:B10:01) can be classed as a low-magnesia, high-potash (LMHK) soda-lime-silica glass (Henderson, 1985: 271–275). The round blue and yellow beads can be classed as a high-magnesia (HMG) soda-lime-silica glass. The fourth glass type, represented by the fragmentary bead from burial 9 in kurgan 23 at cemetery 2, is a leaded soda-lime-silica glass.

As can be expected, each of these different compositional groups reflects the use of different fluxing agents. LMG glasses are believed to have been produced using natron, seaweed, or sea salt as the fluxing agent, while the HMG glasses are believed to have been produced using soda plant ash (Brill, 1988: 258; Henderson, 1985: 273–275; Wypyski, 1992: 282). LMHK glass is believed to have been produced with saltpetre or a purified soda plant ash flux (Sen & Chaudhuri, 1985: 34; Wypyski, 1992: 283).

As for the other major and minor elements, the alumina content ranges from 1·50% to 5·00%. The iron content, as Fe$_2$O$_3$, ranges from 0·80% to 12·00%. Depending on the type of glass, the manganese content ranges from 0·050% to 0·800% MnO. The low manganese concentration, coupled with the low MnO:Fe$_2$O$_3$ ratio, indicates that manganese was not intentionally added as a decolouant in any of the glasses (Brill, 1988: 277). Strontium and titanium, common impurities in sand, are all present in the glass beads (Brill, 1988: 263; Sanderson *et al.*, 1984: 54). The strontium content ranges from 60 ppm to 480 ppm SrO. The titanium content ranges from 0·110% to 0·542% TiO$_2$. Figure 2 suggests that at least five sources of sand were used to manufacture the glass beads.

Both cobalt and copper are used as colourants in the blue glass beads. The round, blue beads from burial 1 in kurgan 8 at cemetery 1 contain an average of 0·765% ± 0·022% CuO and no detectable amounts of cobalt. The two pieces of blue LMG glass contain both cobalt and copper in sufficient amounts for either one to have produced the blue colour (Caley, 1962: 26, 74–76; Farnsworth & Ritchie, 1938: 160). The blue LMHK glass (P02:K23:B10:01) was also coloured with cobalt and copper.
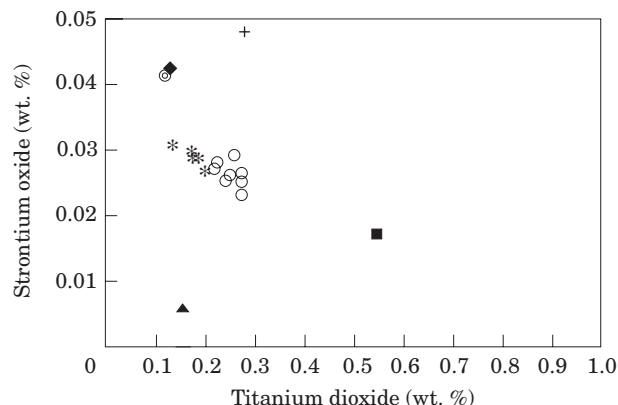
Figure 2. Plot of the titanium dioxide content versus the strontium oxide content. Visually there appears five to six groups. Key as for Figure 1.

Excluding the leaded glass bead, lead is found only at trace levels in these beads. The lead content ranges from 0·001% PbO to 0·029% PbO. Nickel, niobium, rubidium, yttrium, zinc and zirconium were also found at trace levels in these glasses. Gallium and thorium were searched for, but not found at detectable levels in the glass beads.

Multivariate analysis

The Al_2O_3, CaO, Fe_2O_3, K_2O, MgO and Na_2O contents were treated by cluster analysis and discriminant analysis to see if the beads were made from similar or different glass recipes. While four types of glass can be recognized on the basis of the major elements, it is quite possible that several distinct recipes were used to manufacture the glass beads. The above listed elements are used since they are the major constituents of glass; the trace elements are not used since they can act as colourants. Silica is not included in the statistical analysis since it is inversely correlated with the other elements and would skew the final results (Baxter, 1994: 72–77).

The data were not transformed or standardized before the cluster analysis. The dendrogram in Figure 3 was created using Ward's method and the squared Euclidean distance to evaluate the objects' similarities. As can be seen, anywhere from two to five chemical groups can be identified in the data.

Discriminant analysis was done to verify the validity of five different chemical recipes being represented in the data. Linear discriminant analysis, assuming equal probabilities of group membership and using the with-in group covariance matrix for the above listed oxides, correctly assigned 100% of the specimens to their appropriate group (Figure 4). The same result was obtained using the $\log_{10}$ transformed values of the oxides in the linear discriminant analysis. Because some of the groups contain only one member, "jack-knifing" or cross-validation could not be run.
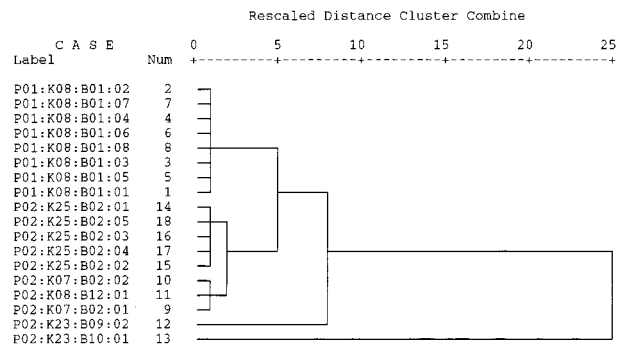

Figure 3. Dendrogram showing the results of the cluster analysis. The Al_2O_3, CaO, Fe_2O_3, K_2O, MgO and Na_2O contents were clustered using Ward's method and the squared Euclidean distance.
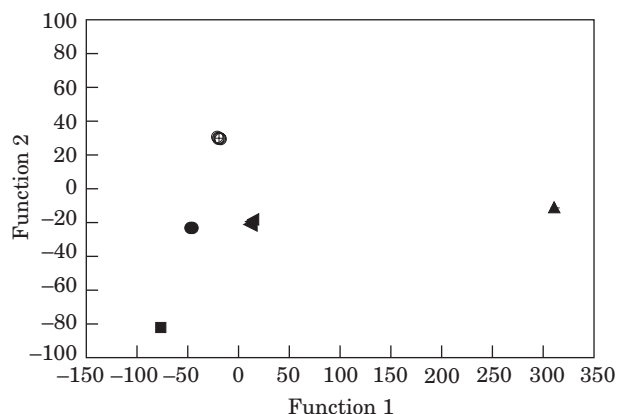

Figure 4. Plot of the first two linear discriminant functions. Linear discriminant analysis successfully separates all the observations into their correct groups. Chemical groups: +, Group centroids; ◄, Group 5; ▲, Group 4; ■, Group 3; ●, Group 2; ○, Group 1.

Stepwise discriminant analysis with the goal of maximizing the Mahanobolis distance between groups, probability of F-to-enter equal to 0·05, and probability of F-to-remove equal to 0·10, correctly classified 100% of the glass beads into their appropriate groups. The Al_2O_3, Fe_2O_3, K_2O, MgO and Na_2O contents were identified as the oxides required to correctly classify the specimens.

Discussion

The results of the cluster analysis and discriminant analysis indicate that there are five distinct glass recipes represented in the chemical analyses. Table 3 contains the average composition of the five chemical groups.

Chemical group 1 consists of the eight blue, round beads recovered from burial 1 in kurgan 8 at Pokrovka cemetery 1. While HMG glasses can be found in Central Asia and the Near East during the first millennium BC and the first millennium AD, the high alumina and low lime content point to an origin in the Indian subcontinent (Bhardwaj, 1987; Brill, 1987: 4, 9, 10;

Table 3. Average chemical composition of each chemical group of glass

Element	Group 1 (N=8) HMG	Group 2 (N=3) LMG	Group 3 (N=1) Type of glass Pb-glass	Group 4 (N=1) LMHK	Group 5 (N=5) HMG
Al_2O_3	4·60 ± .07	2·19 ± .25	1·55	1·40	1·49 ± .01
CaO	5·42 ± .11	6·91 ± .51	2·83	2·91	6·92 ± .24
Fe_2O_3	0·85 ± .01	1·28 ± .11	11·68	0·87	1·37 ± .29
K_2O	3·51 ± .04	1·03 ± .47	0·41	19·59	3·42 ± .03
MgO	2·58 ± .17	0·70 ± .30	0·34	0·35	3·18 ± .09
Na_2O	19·16 ± .21	15·23 ± 1·93	11·44	0·25	15·97 ± .45
SiO_2	60·89 ± .47	70·18 ± 2·46	53·30	72·34	66·35 ± .37
CoO	n.d.	0·011 ± .011	0·014	0·004	n.d.
CuO	0·765 ± .022	0·185 ± .031	0·261	0·018	0·006 ± .001
MnO	0·053 ± .002	0·390 ± .377	0·030	0·017	0·157 ± .021
NbO_2	n.d.	0·001 ± .000	n.d.	0·001	0·001 ± .001
NiO	n.d.	0·001 ± .001	0·005	0·006	0·003 ± .002
PbO	0·021 ± .005	0·049 ± .060	17·25	0·011	0·002 ± .001
Rb_2O	0·004 ± .001	0·002 ± .001	n.d.	0·010	0·003 ± .002
SrO	0·026 ± .002	0·043 ± .004	0·017	0·006	0·029 ± .001
TiO_2	0·247 ± .022	0·171 ± .089	0·542	0·153	0·168 ± .024
Y_2O_3	0·001 ± .000	0·001 ± .001	n.d.	0·001	0·001 ± .001
ZnO	0·010 ± .003	0·009 ± .003	0·017	0·007	0·009 ± .004
ZrO_2	0·008 ± .001	0·008 ± .005	0·018	0·010	0·004 ± .001

All values are in weight percent.
N = the number of individuals in each group.
The chemical groups were determined by cluster analysis and verified with linear discriminant analysis.

Brill, 1989; Matveeva, 1993: 160; Wypyski, 1992: 282, 283).

LMG glasses comprise chemical group 2. LMG glasses can be found in a broad band stretching from the central Mediterranean to eastern Siberia (Abdurazakov, 1987, 38–41; Brill, 1987: 3; Caley, 1962: 69–82; Galibin, 1983; Matveeva, 1993:160; Naoumov, 1962 Sayre & Smith, 1961:1825). Soda-lime-silica glass production centres and workshops dating to the second half of the first millennium BC have only been found in the Crimea and Georgia (Abdurazakov, 1987:39; Belov, 1965; Ugrelidze, 1989), Egypt (Caley, 1962:69–82) and Syria-Palestine (Barag, 1985: 60–88, 101–105). While the cluster analysis indicates this is a single group, the plot of SrO versus TiO_2 (Figure 2) indicates that at least two different sources of sand were used in the manufacture of the LMG glass beads. We interpret this as evidence for the LMG glass beads coming from at least two different manufacturing centres.

The leaded-soda-lime-silica glass from burial 9 in kurgan 23 at Pokrovka cemetery 2 is the sole member of group 3. Chemical analyses indicate that the Chinese consistently produced leaded-soda-lime-silica glass from the Warring States period onwards (Caley, 1962:38–50, 89–91; Ritchie, 1937; Shi, He & Zhou, 1989; Yoshimizu, 1992:125–126; Zhang, 1987). The low BaO content in this particular bead points to it being manufactured in the Han period or later (Caley, 1962:90, 91; Ritchie, 1937:219; Seligman, Ritchie & Beck, 1936).

The single LMHK glass fragment comprises chemical group 4. LMHK glasses have been found in first millennium BC contexts in the Pazyryk burials in the

Altai (Galiban, 1993), at a variety of burials in Gansu, Guangdong, Guangxi and Yunnan provinces in China (Shi, He & Zhou 1986, 1987, 1989), at the sites of Kausambi, Taxila and Rajghat in the Indian sub-continent (Sen & Chaudhuri, 1985:24, 110–118), Tagar period burials throughout Siberia (Galiban, 1983), and insular Southeast Asia (Basa, Glover & Henderson, 1991; Harrisson, 1968). Where glass like this was originally manufactured is uncertain; Chinese scholars favour a location in southeast China, while others argue for manufacture somewhere in South Asia or Southeast Asia (Basa, Glover & Henderson, 1991; Galibin, 1993, Glover & Henderson, 1995; Harrisson, 1968; Shi, He & Zhou 1987, 1989).

The yellow glass beads from burial 2 in kurgan 25 at Pokrovka cemetery 2 form the fifth chemical group. Unlike group 1, these HMG glasses contain low amounts of alumina. These beads could have been made in the Near East or the Indian subcontinent (Brill, 1987).

The presence of glass beads from such diverse sources are evidence of an exchange or trade network running not only from east to west, but also from north to south. While past researchers have focused on contact between the Mediterranean world and China, the blue HMG glass beads from Pokrovka attest to the Indian subcontinent's presence in the exchange/trade networks. The Maruyan Empire, c. 325–185 BC, is recorded as having trade relations with states in Afghanistan, Bactria, China and Persia (Allchin, 1995: 194). Furthermore, both archaeological and literary evidence points towards a thriving glass industry in the Maruyan Empire (Dikshit, 1964/1965:64–67).

How the overland trade worked and the role of the nomadic peoples in it is uncertain though. Gorbunova (1993/1994) has proposed that the nomadic groups acted as intermediaries, possibly moving the goods with their herds. Alternatively, since the trade routes between the Black Sea states to Transoxania and China ran through Sarmatian territory, others (Sulimerski, 1970:92–143; Zadneprovisky, 1994:466) see the Sarmatians as exacting tribute from the overland traders. A large scale study of glass and exotic metal-work across Kazakhstan, the southern Russian steppes and Uzbekistan could possibly elucidate which of these models, or some other, is correct.

Conclusion

The glass analyses presented here demonstrate the long distance trade/exchange connections of the Sarmatians. Multivariate data analysis reveals five different glass recipes in the compositional data. The leaded glass bead had its origin somewhere in China, the LMG glass is evidence of contact with the Eastern Mediterranean and the high alumina HMG glass is evidence of contact with the Indian subcontinent. Whether this trade/exchange was direct or through middlemen is uncertain; glass beads are small and portable, and they could have been carried and exchanged by intermediaries. As further analyses are carried out, it may be possible to elucidate the role the Sarmatians played in the long distance exchange/trade networks along the "Silk Road".

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